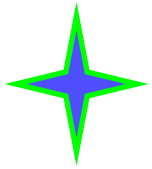




SCU



微波化学对经典电磁理论 的挑战

黄卡玛

四川大学电子信息学院

Outline

1. 微波化学中的非线性响应
2. 微波对氢键的作用
3. 化学极化增量
4. 化学反应中的波动方程
5. 结论

微波化学中的非线性响应



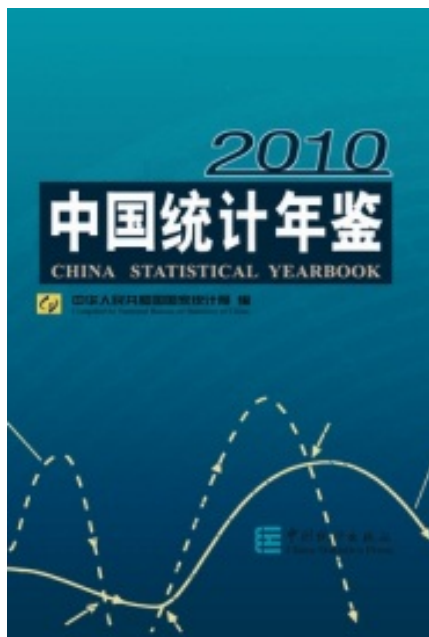
Energy saving and emission reduction

微波化学中的非线性响应

其中**五个**行业涉及加热处理



石油加工炼焦加工业



非金属矿物制品



黑色、有色金属



化学原料及化学制品
制造业

微波化学中的非线性响应

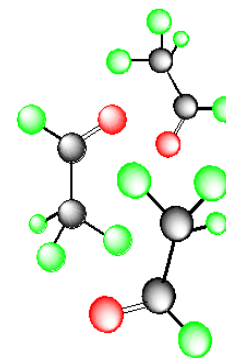
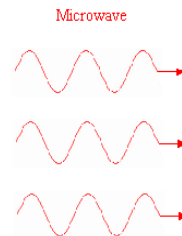
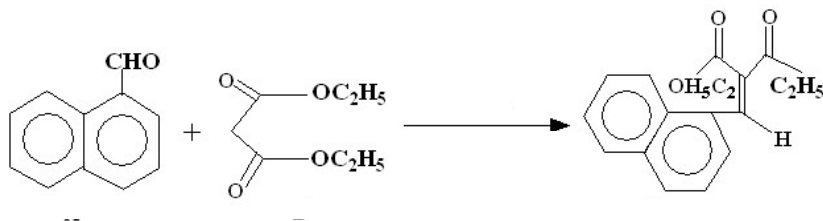
Arrhenius equation

$$k = A \exp\left(-\frac{E_0}{RT}\right)$$



微波化学中的非线性响应

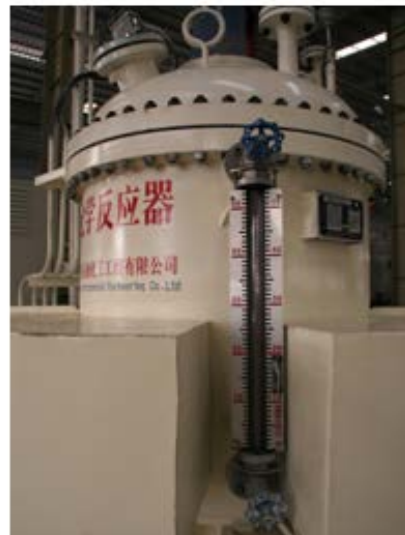
Condensation reaction of α -naphthaldehyde and diethyl malonate



Heating methods	Time-consuming (min)	Abortion rate (%)	Energy consumption (KJ/mol)
Conventional heating	1440	44.7	4.9
Microwave heating	5	78	0.24

Microwave heating in chemical industry has shown a good advantage of energy saving and emission reduction.

微波化学中的非线性响应



微波化学中的非线性响应



Microwave treatment of sewage

微波化学中的非线性响应



微波竹炭生产装备

微波化学中的非线性响应

Mobile Microwave Assisted Biomass Pyrolysis/Gasification System

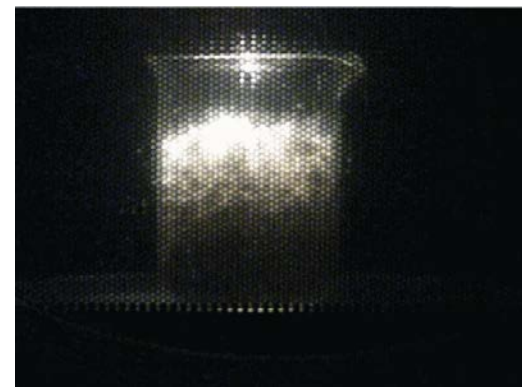


微波化学中的非线性响应

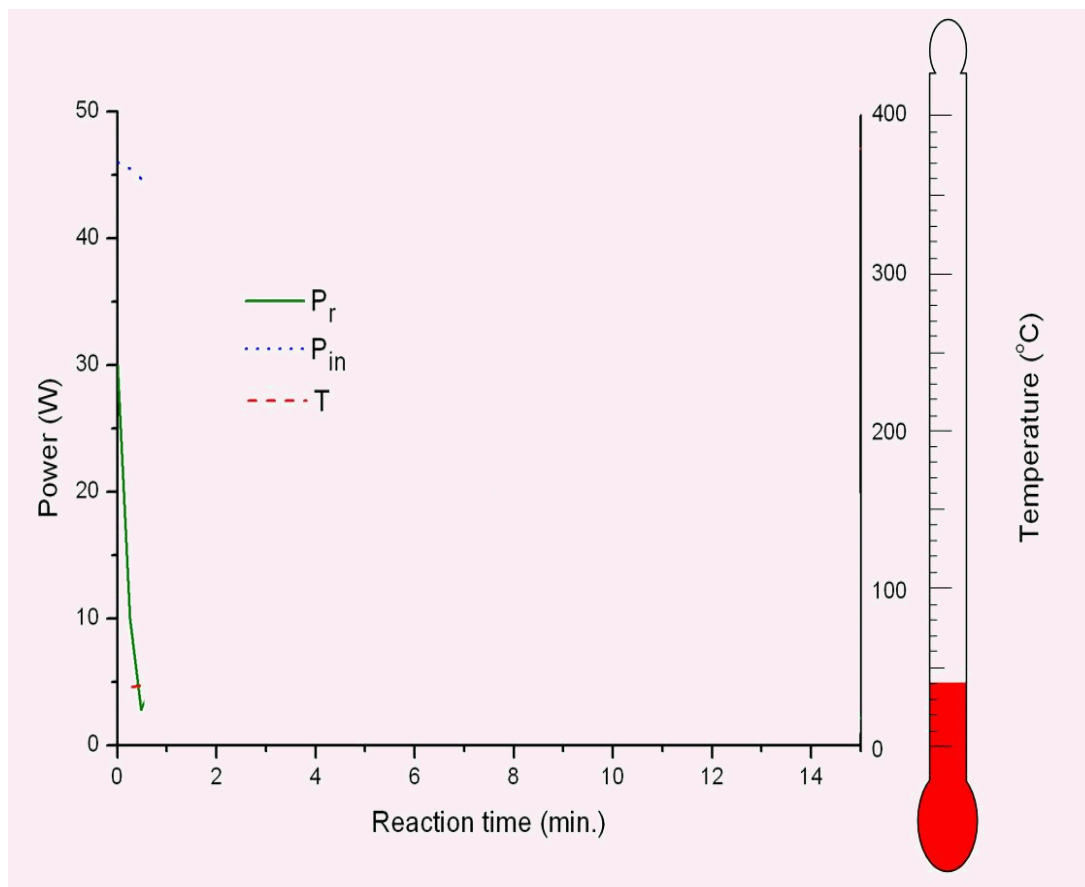
- Thermal-runaway causes reactants to be burned out.



- Inhomogeneous heating causes the explosion during the reaction.



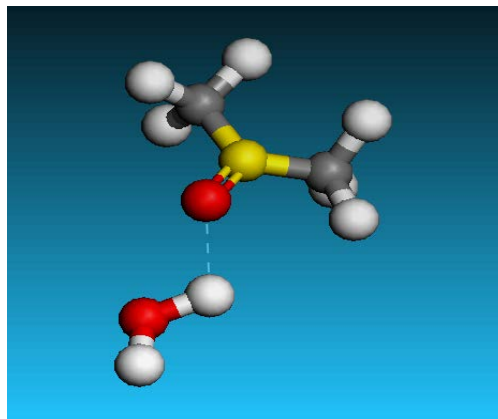
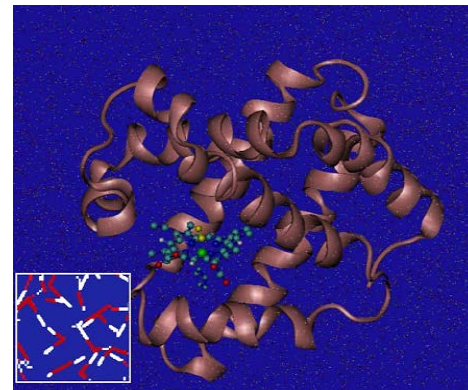
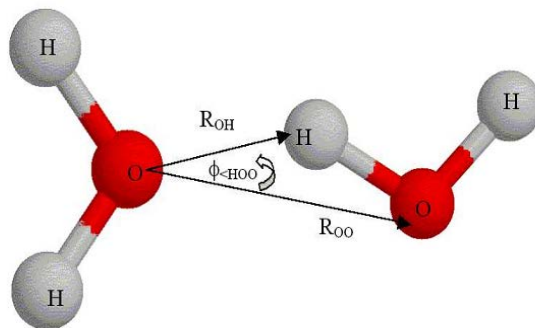
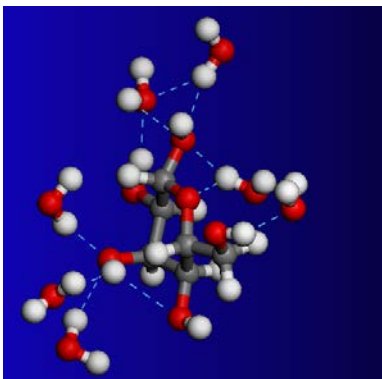
微波化学中的非线性响应



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微波对氢键的作用



微波对氢键的作用

Microwave photon (2450MHz)	Covalent bond	Metallic bond	Ionic bond	Hydrogen bond
10^{-5} eV	5eV	2.4eV	7.6eV	0.04~0.44eV

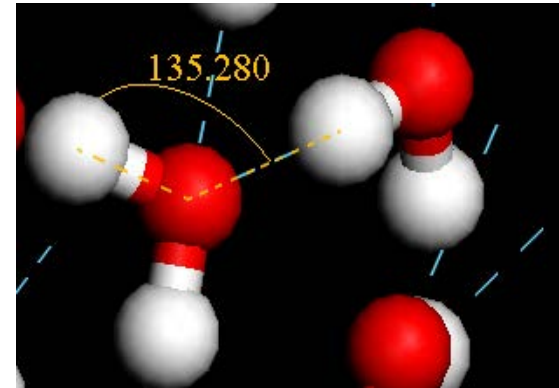
**Heated argument on
microwave non-thermal effects**

Molecular Dynamic Simulation

External microwave field:

$$\vec{E}(t) = E_{\max} \cos(\omega t)(0\vec{e}_x + 0\vec{e}_y + 1\vec{e}_z)$$

$$\vec{H}(t) = H_{\max} \sin(\omega t)(0\vec{e}_x + 1\vec{e}_y + 0\vec{e}_z)$$



Intermolecular LJ potential function :

$$u_{ij}(r) = 4\varepsilon_{ij} \left[\left(\sigma_{ij} / r \right)^{12} - \left(\sigma_{ij} / r \right)^6 \right] + q_i q_j / 4\pi\varepsilon_0 r$$

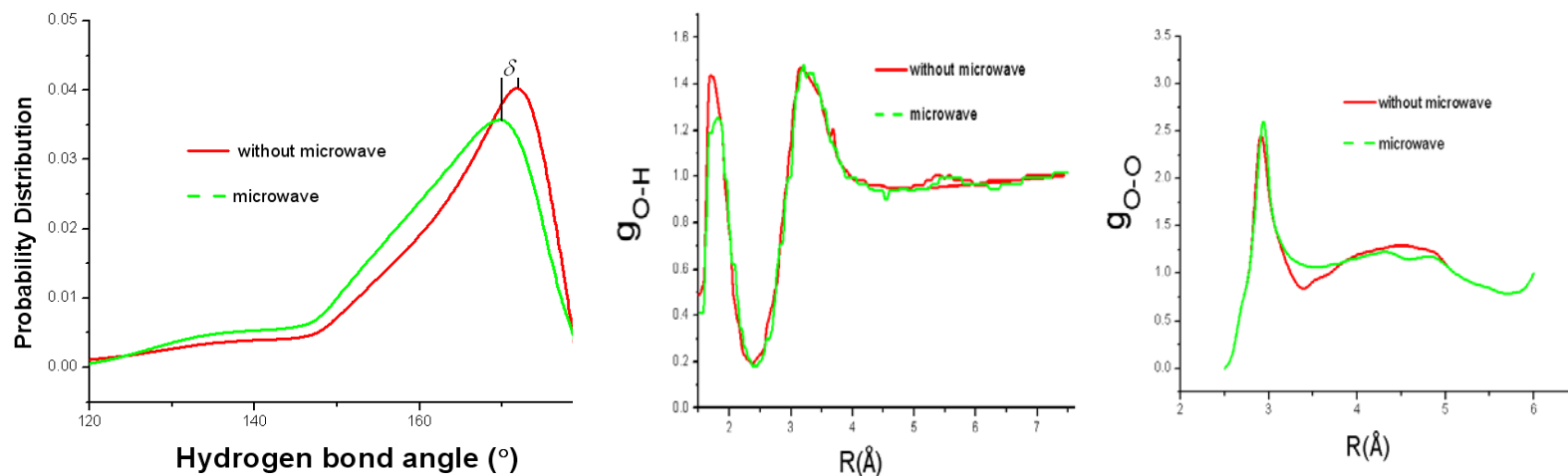
SPC model parameters:

	σ/nm	$\varepsilon/(kJmol^{-1})$	$q(a.u)$
O	0.65	0.3165	-0.82
H	0.0	0.0	0.41

Hydrogen bonding definition :

- Two water molecules are chosen as being hydrogen bonded distant $O-O \leq 3.5 \text{ \AA}$
- 2 simultaneously the $O-H\dots O$ angle $\leq 30^\circ$

Hydrogen bond variation in microwaves



J. Phys. Chem. A 2010, 114, 1185–1190

1185

Dielectric Properties of *N,N*-Dimethylformamide Aqueous Solutions in External Electromagnetic Fields by Molecular Dynamics Simulation

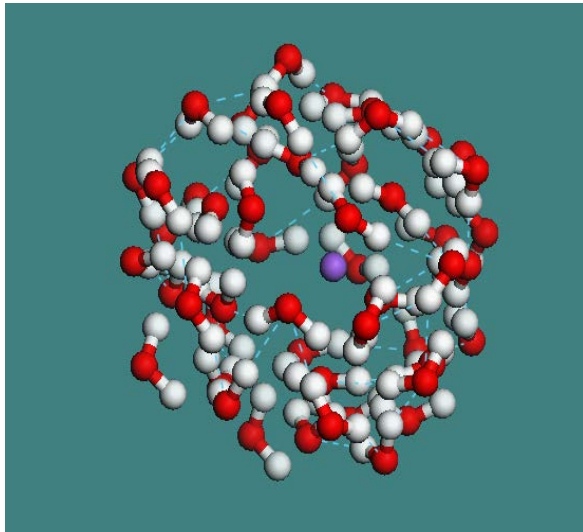
LiJun Yang, KaMa Huang,* and XiaoQing Yang

College of Electronics and Information Engineering, Sichuan University, Chengdu, 610064, P.R. China

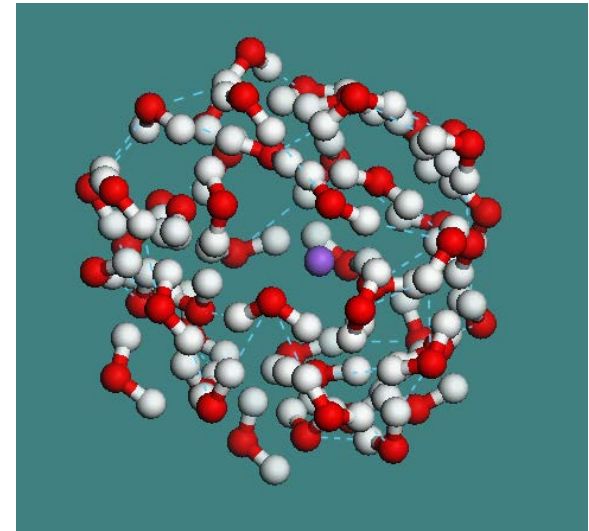
Received: October 13, 2009; Revised Manuscript Received: November 18, 2009



Variation of Na^+ cluster in microwaves



Structure 1



Structure 2

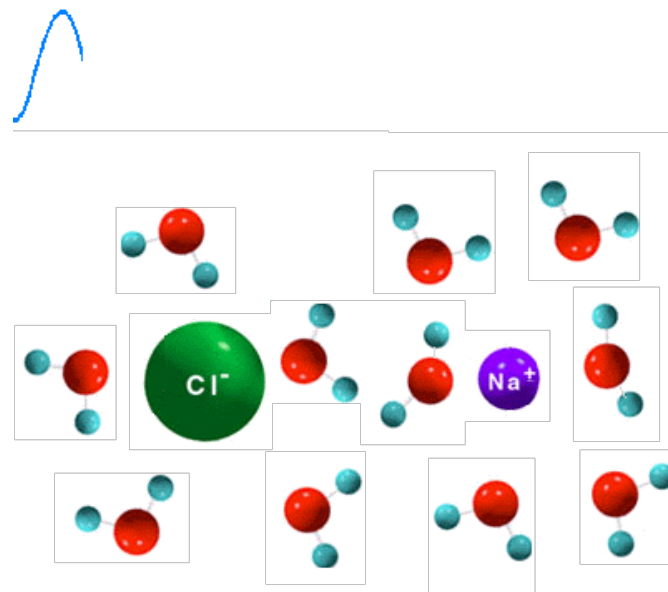
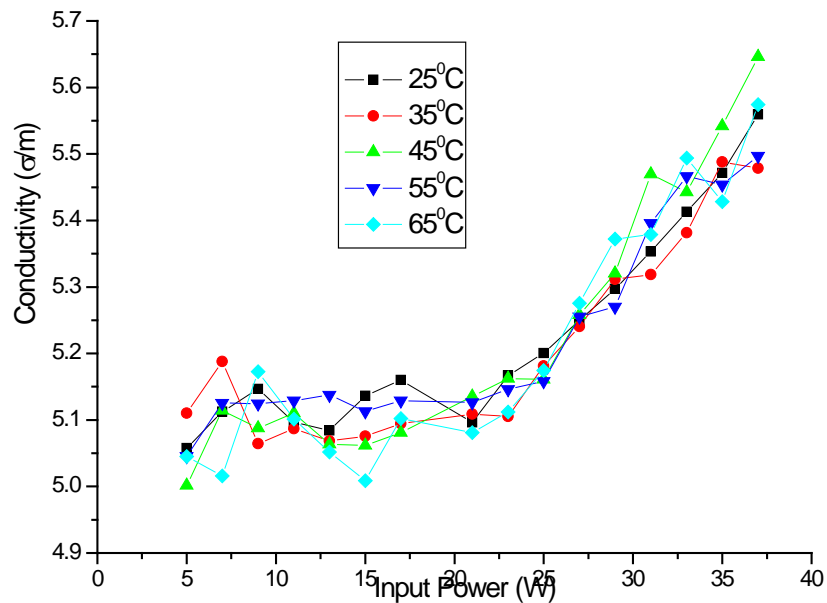
Na^+ Cluster

Total binding energy: $E_1 = -19.2719959$ au,

Total binding energy: $E_2 = -19.2719601$ au,

Electric conductivity of solution changed by

MW



J. Phys. Chem. B 2010, 114, 8449–8452

8449

Electric Conductivity in Electrolyte Solution under External Electromagnetic Field by Nonequilibrium Molecular Dynamics Simulation

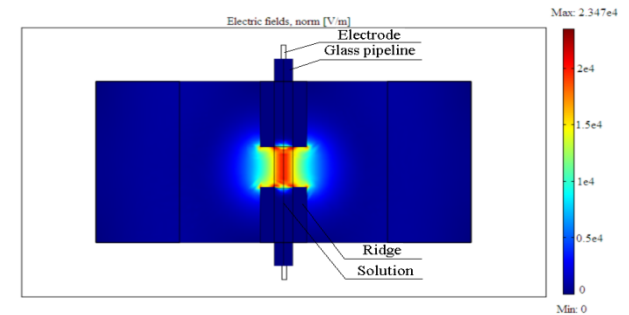
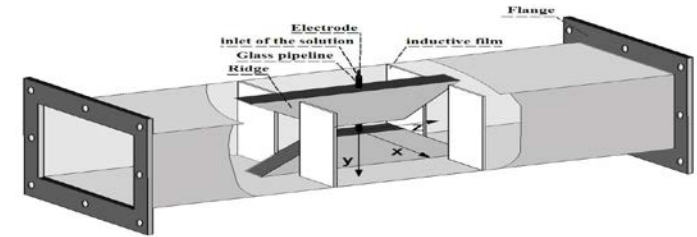
Lijun Yang and KaMa Huang*

College of Electronics and Information Engineering, Sichuan University, Chengdu, 610064, People's Republic of China

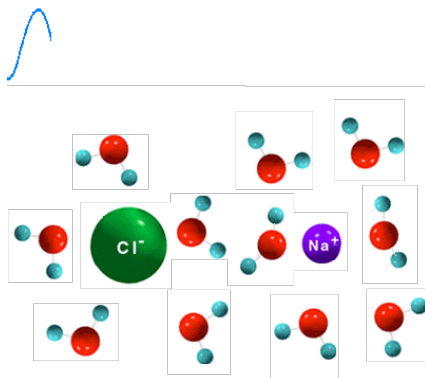
Received: March 23, 2010



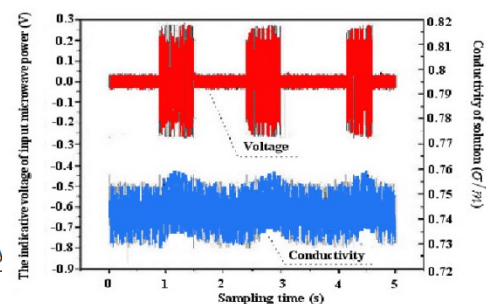
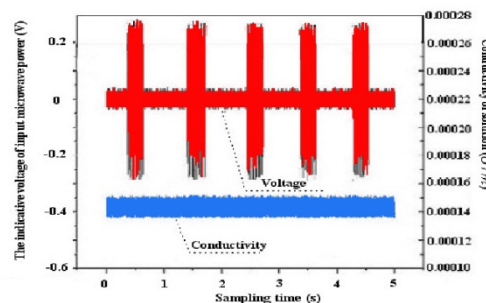
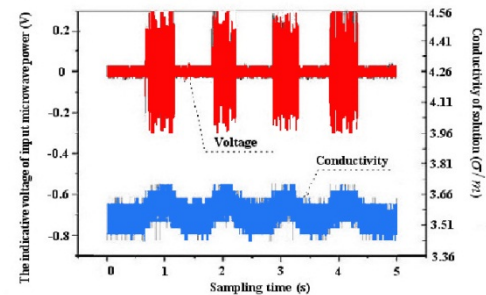
Measurement of small EC change



Measurement of small EC change



The measured relative EC variations				
		Temperature		
Concentration		10 ⁰ C	16 ⁰ C	22 ⁰ C
0.1 mol/L		2.1%	1.3%	0.6%
0.5 mol/L		4.0%	1.7%	0.9%



PAPER

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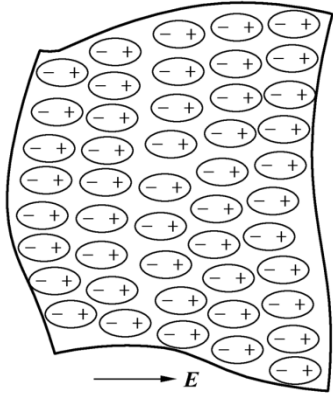
Experimental evidence of a microwave non-thermal effect in electrolyte aqueous solutions

Kama Huang,* Xiaoqing Yang, Wei Hua, Guozhu Jia and Lijun Yang

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Effective permittivity



$$\langle P \rangle = \frac{\sum p e^{-u/kT}}{\sum e^{-u/kT}}$$

$$\mathbf{P} \approx ? \mathbf{E}$$

Macroscopic polarization:

$$\chi = \frac{N\alpha}{\varepsilon_0} = \frac{N}{\varepsilon_0} \left(\alpha_e + \alpha_i + \frac{p_0^2}{3kT} \right)$$

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi) \mathbf{E}$$

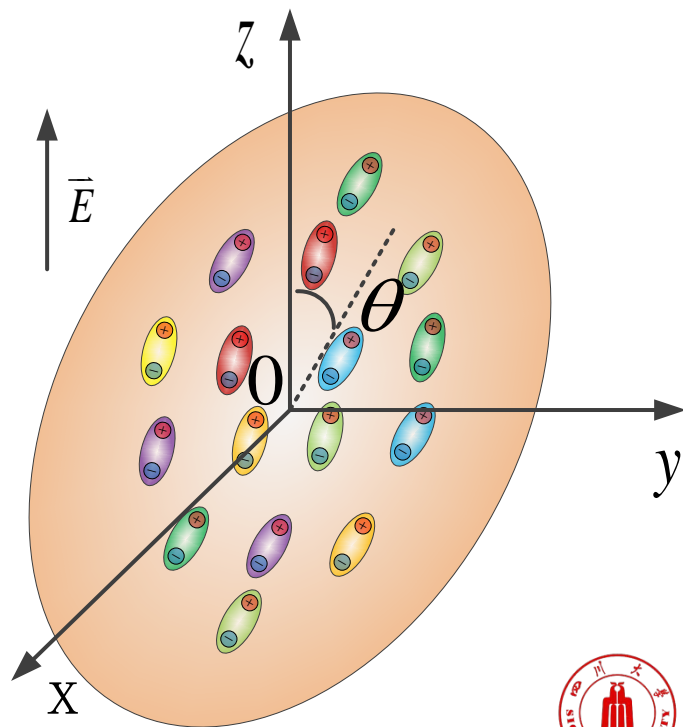
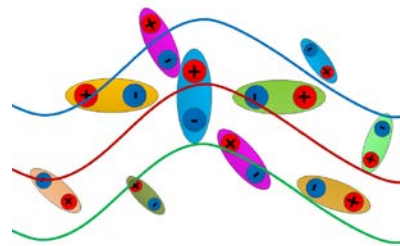
$$\varepsilon = \varepsilon_0 (1 + \chi) = \varepsilon_0 + N \left(\alpha_e + \alpha_i + \frac{p_0^2}{3kT} \right)$$

化学极化增量

在电场作用下，按玻尔兹曼分布律，极性分子的偶极矩 μ 在 θ 和 $\theta + d\theta$ 之间的取向几率与 $\exp(-\mu_0 E / kT) d\Omega$ 成正比，可以得到电场方向的平均偶极矩

$$\bar{\mu} = \mu L\left(\frac{\mu_0 E}{kT}\right),$$

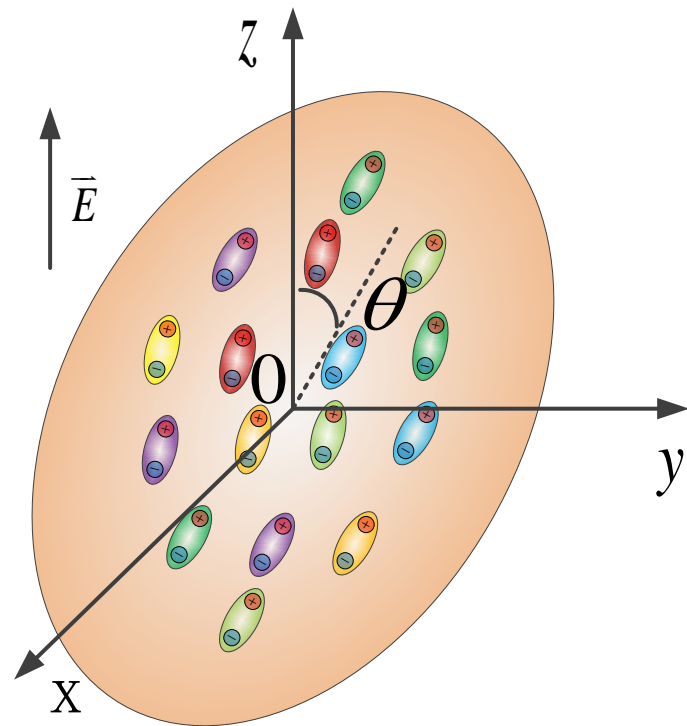
L 为 Langevin 函数。



化学极化增量

若 $\mu_0 E \ll kT$ (μ_0 很小或者 E 很小),
只考虑极性分子的取向极化且不
考虑分子间相互作用, 可以得到
极化强度和相对介电系数

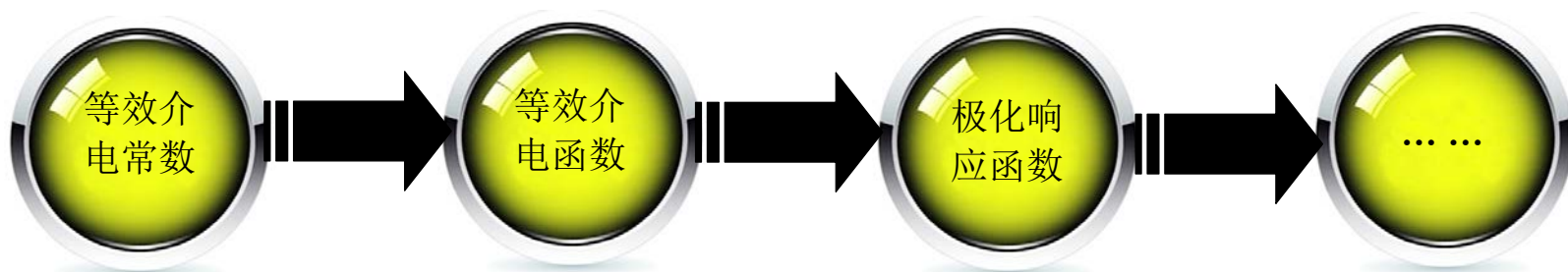
$$\bar{P} = \frac{N\mu^2}{3kT} \bar{E} = \varepsilon_0 (\varepsilon_r - 1) \bar{E}$$



化学极化增量

在绝大多数情况下，CRS中分子不再满足Boltzmann分布。

此时应该不存在**介电常数**的概念，极化强度是电场的复杂时域响应。



化学极化增量

对于一般电介质，如果满足条件：

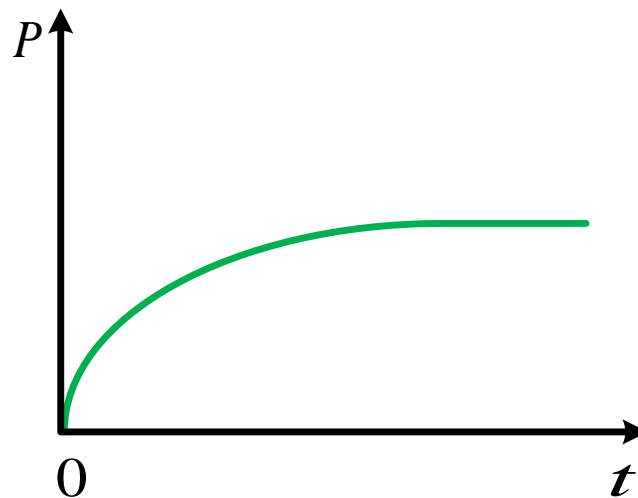
- Causality
- Linear superposition
- Markov process

$$\bar{P}(t) = \beta(t) * \bar{E}(t)$$

$$\beta(t) = \frac{1}{\tau} e^{-t/\tau} \quad (\text{响应函数})$$

$$\tau = \frac{\hbar}{kT} \exp\left(\frac{\Delta G}{RT}\right) \quad (\text{Eyring方程})$$

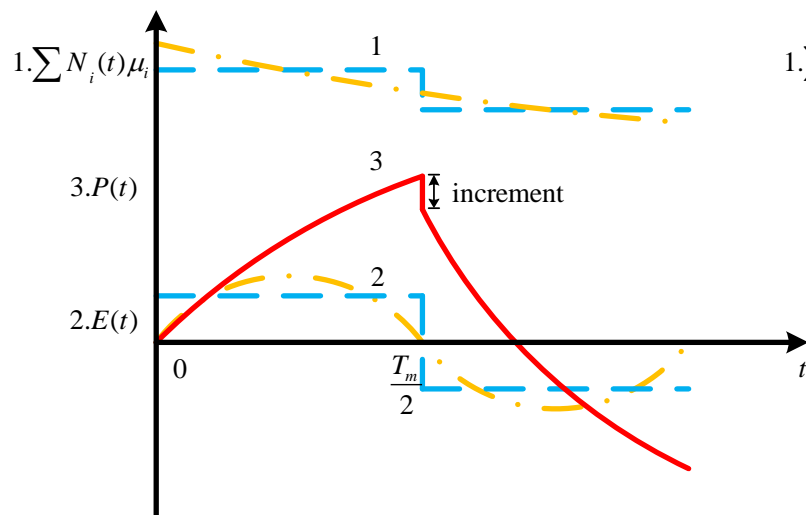
$$\Delta G = \Delta H - T \cdot \Delta S$$



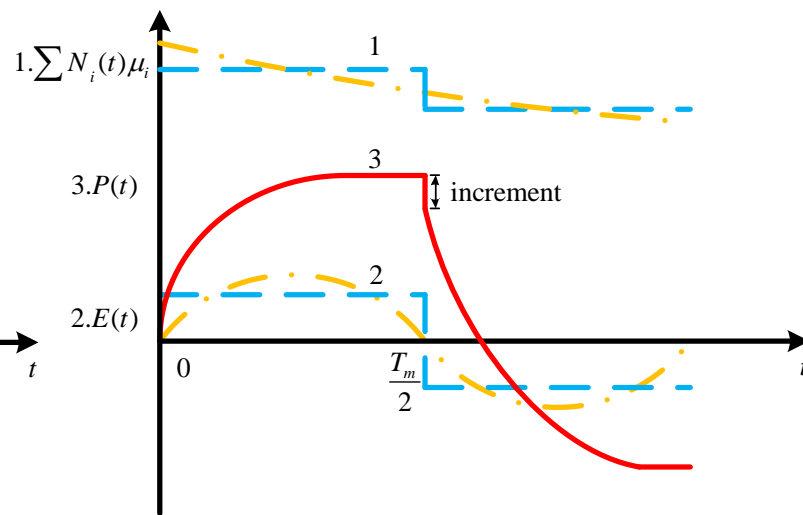
在恒定电场作用下一般电介质
极化强度变化

化学极化增量

基本思想：局域平衡假设



$$T_{ch} > \tau > \frac{T_m}{2}$$



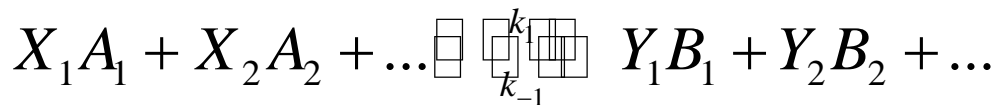
$$T_{ch} > \frac{T_m}{2} > \tau$$

正弦电场作用下，CRS极化强度变化

得到CRS极化强度的表达 $\vec{P} = \vec{P}_{mix} + \Delta\vec{P}$

化学极化增量

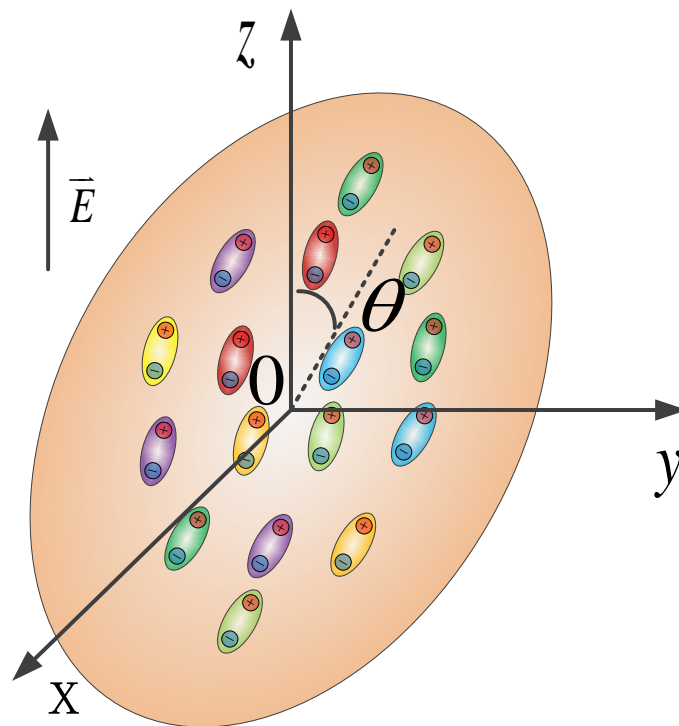
一般化学反应



在电场作用下，各个物质浓度的分布函数

$$dC_{A_i} = \gamma_{A_i}(E, \theta, t) d\Omega$$

$$dC_{B_j} = \gamma_{B_j}(E, \theta, t) d\Omega$$



化学极化增量

在正弦电场作用下，反应过程引起的极化增量

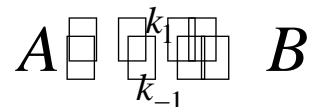
$$\begin{aligned} \Delta P(t) = & g_a N_A \int_0^\pi 2\pi \sin \theta \cos \theta \\ & \times \left(\sum_i \mu_{A_i} \left(\gamma_{A_i}(E, \theta, t) - \gamma_{A_i}(E, \theta, t - T_s) \right) \right. \\ & \left. + \sum_j \mu_{B_j} \left(\gamma_{B_j}(E, \theta, t) - \gamma_{B_j}(E, \theta, t - T_s) \right) \right) d\theta \end{aligned}$$

其中 g_a 为系数， N_A 为阿伏伽德罗常数

$$T_s = \frac{T_m}{2}, \quad t = nT_s, n = +1, +2, \dots$$

化学极化增量

考虑一个简单的化学反应

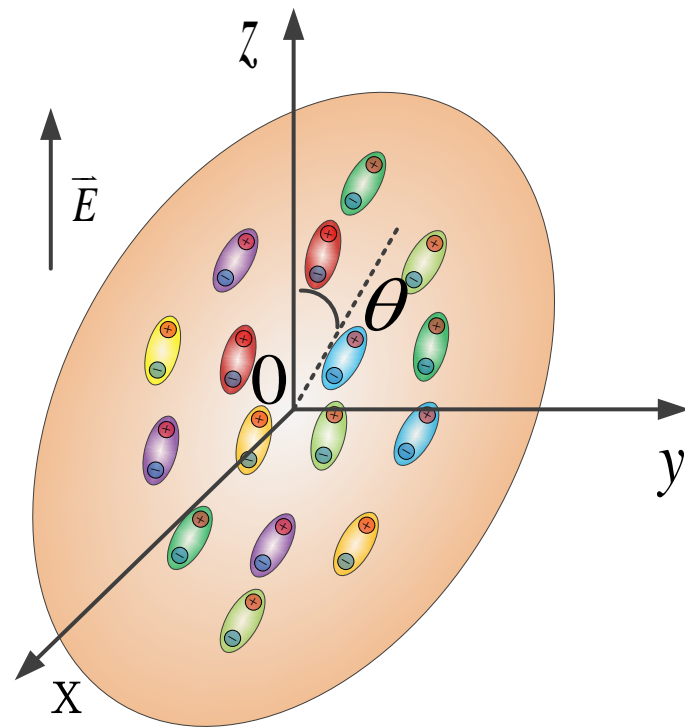


假设A与B旋转扩散系数均为 D_r ，
反应的每一瞬间及任意小体积
内体系处于麦克斯韦分布中，
质量守恒方程为

$$\frac{\partial \gamma_A}{\partial t} = -v + D_r \nabla^2 \gamma_A$$

$$\frac{\partial \gamma_B}{\partial t} = v + D_r \nabla^2 \gamma_B$$

$$\text{其中 } v = k_1 \gamma_A - k_{-1} \gamma_B, \quad \nabla^2 \gamma = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \gamma}{\partial \theta} \right)$$



化学极化增量

只考虑电场方向产生的极化强度变化，

令

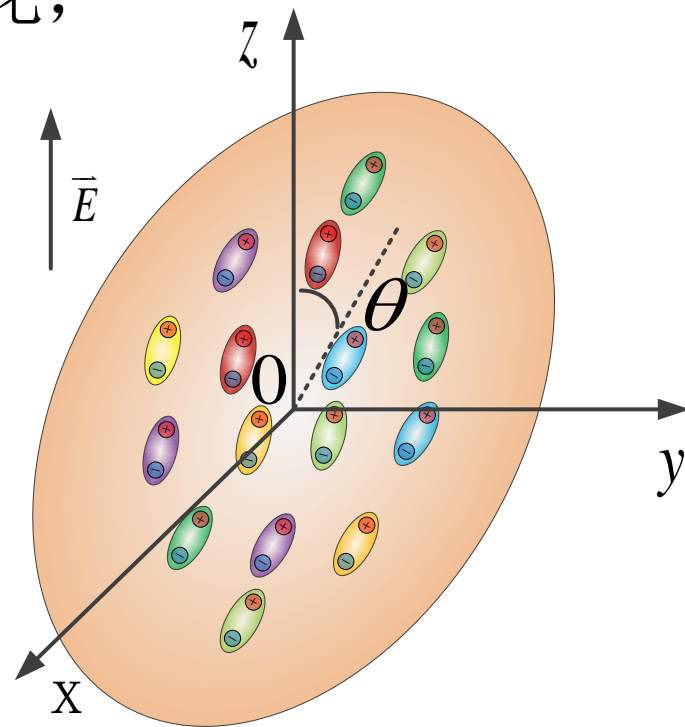
$$\gamma_A = F_A(t) \frac{\mu_A E}{kT} \cos \theta$$

$$\gamma_B = F_B(t) \frac{\mu_B E}{kT} \cos \theta$$

质量守恒方程

$$\mu_A \frac{\partial F_A}{\partial t} = -k_1 \mu_A F_A + k_{-1} \mu_B F_B - 2D_r \mu_A F_A$$

$$\mu_B \frac{\partial F_B}{\partial t} = k_1 \mu_A F_A - k_{-1} \mu_B F_B - 2D_r \mu_B F_B$$



化学极化增量

$$F_A = c_1 e^{-\frac{t}{\tau}} + c_2 e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{ch}}\right)t}, F_B = c_3 e^{-\frac{t}{\tau}} + c_4 e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{ch}}\right)t}$$

得到极化增量

$$\Delta P(t) = \frac{\varepsilon_0 E}{kT} \left((c_1 \mu_A + c_3 \mu_B) e^{-\frac{t}{\tau}} + (c_2 \mu_A + c_4 \mu_B) e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{ch}}\right)t} \right)$$

其中 c_1, c_2, c_3, c_4 为系数, $\tau = \frac{1}{2D_r}, \tau_{ch} = \frac{1}{k_1 + k_{-1}}$,

$t = nT_s, n = +1, +2, \dots$

化学极化增量

若 $\tau_{ch} \ll \tau$

$$\Delta P(t) = \frac{\varepsilon_0 E}{kT} (c_1 \mu_A + c_2 \mu_A + c_3 \mu_B + c_4 \mu_B) e^{-\frac{t}{\tau}}$$

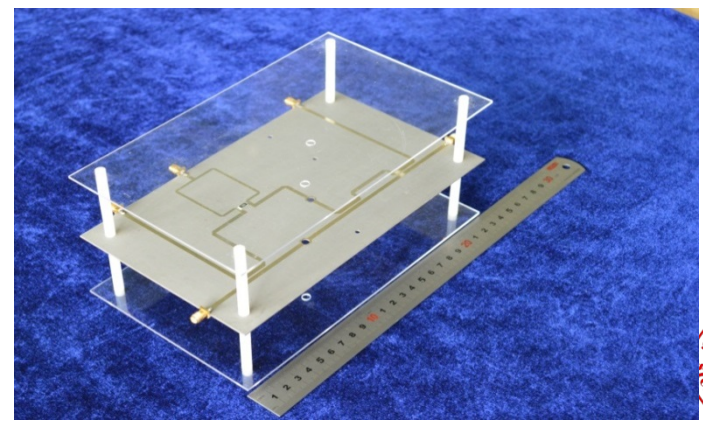
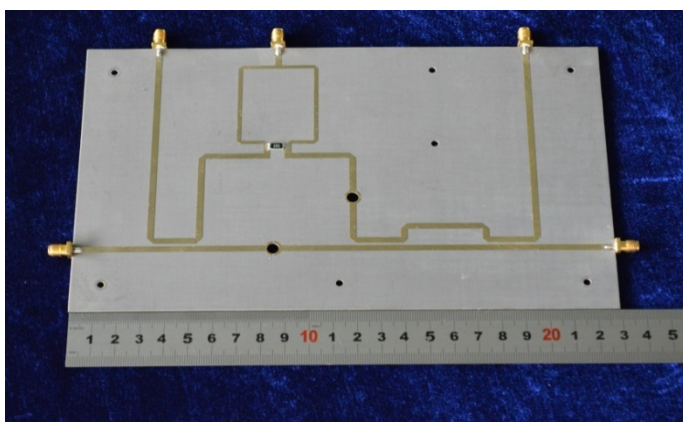
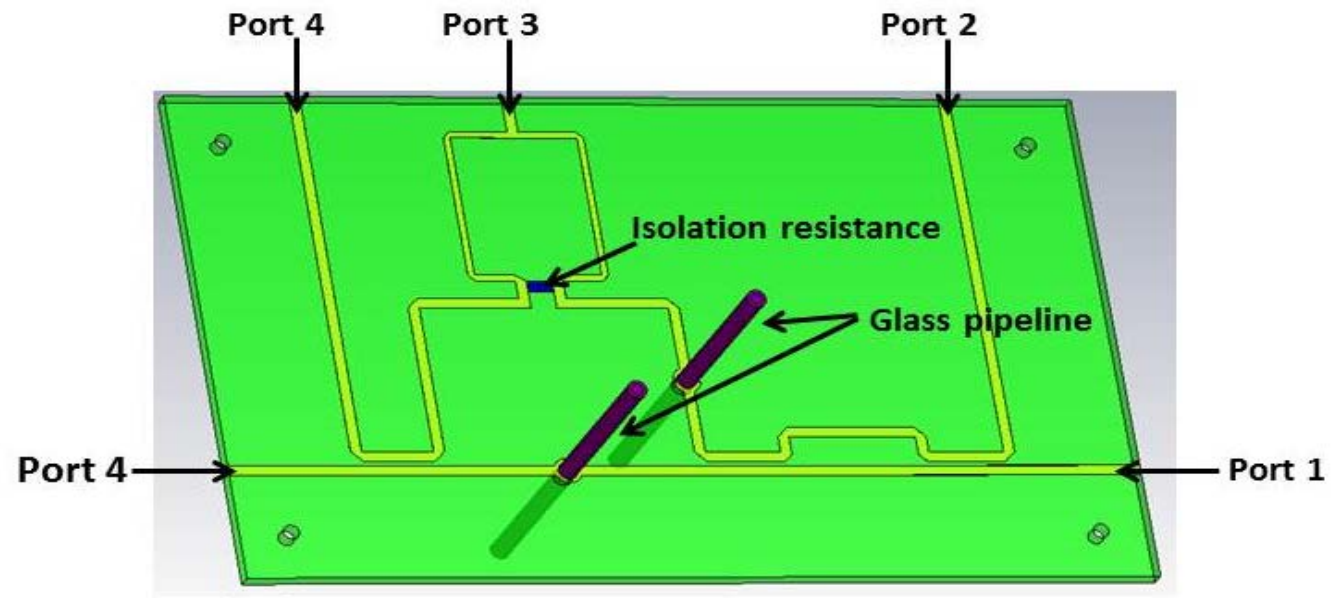
若 $\tau_{ch} \approx \tau$

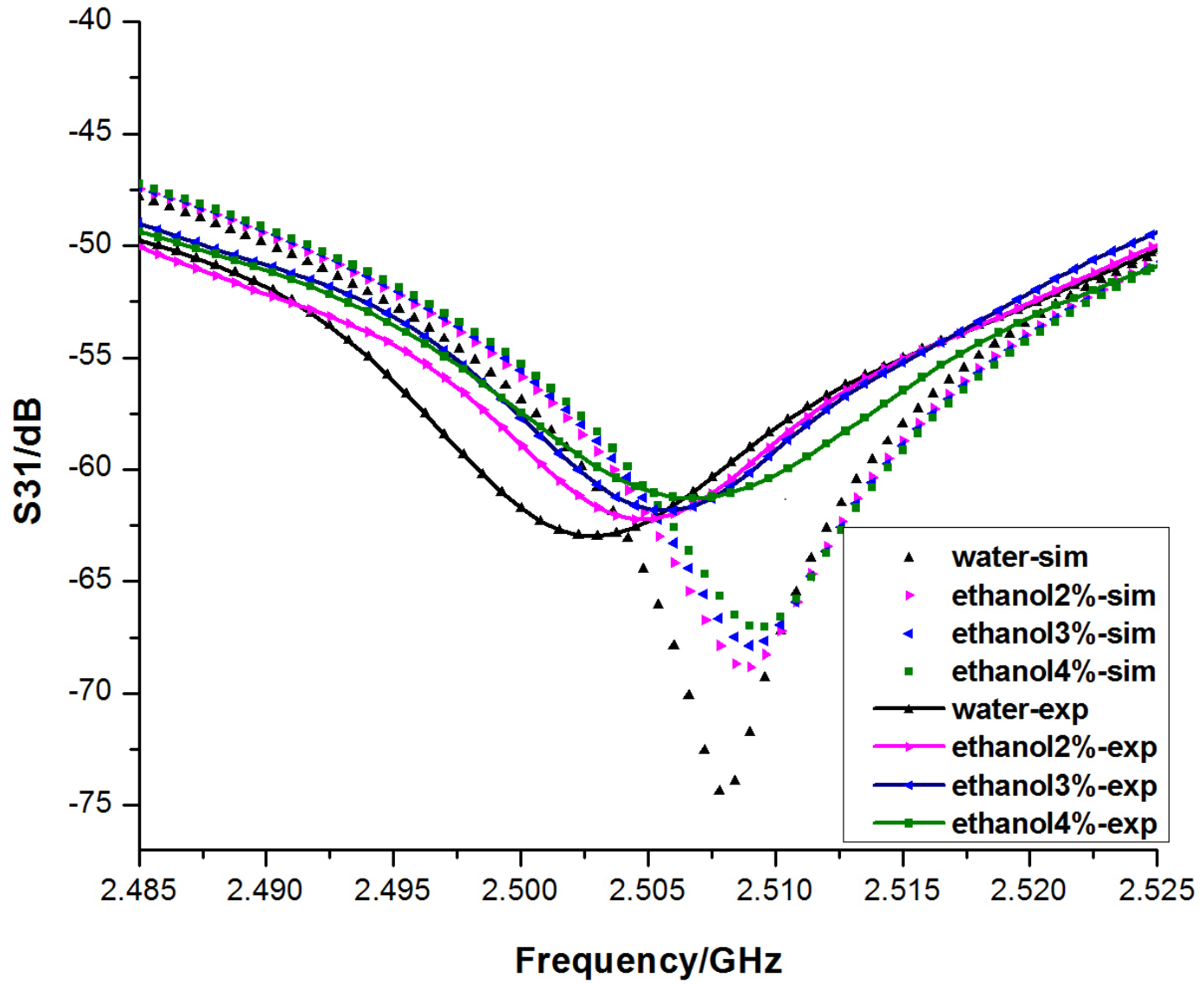
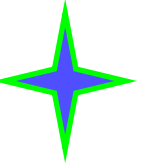
$$\Delta P(t) = \frac{\varepsilon_0 E}{kT} \left((c_1 \mu_A + c_3 \mu_B) e^{-\frac{t}{\tau}} + (c_2 \mu_A + c_4 \mu_B) e^{-\frac{2t}{\tau}} \right)$$

若 $\tau_{ch} \gg \tau$

$$\Delta P(t) = \frac{\varepsilon_0 E}{kT} \left((c_1 \mu_A + c_3 \mu_B) e^{-\frac{t}{\tau}} + (c_2 \mu_A + c_4 \mu_B) e^{-\frac{t}{\tau_{ch}}} \right)$$

化学极化增量





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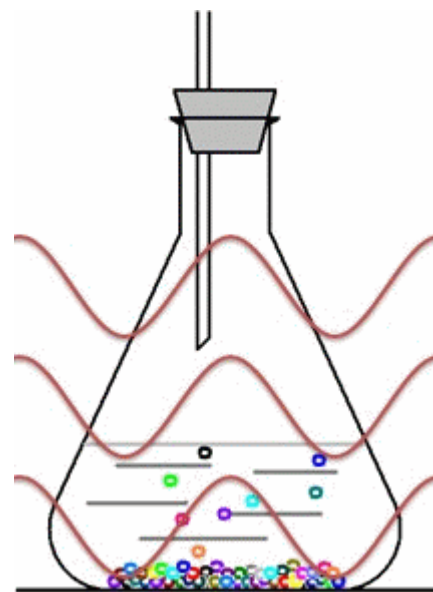
化学反应中的波动方程

麦克斯韦方程组

$$\left\{ \begin{array}{l} \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \vec{\mathbf{J}} \\ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \end{array} \right.$$

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$$

$$\mathbf{P} = \mathbf{P}_{mix} + \Delta \mathbf{P}$$



化学反应中的波动方程

当介质的非均匀性在一个波长内可以忽略时： $\nabla(\nabla \cdot \mathbf{E}) \approx 0$

$$\nabla \times \nabla \times \mathbf{E} = -\mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} - \mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}$$

$$\nabla \times \nabla \times \mathbf{H} = -\mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{H}}{\partial t^2} + \frac{\partial}{\partial t} (\nabla \times \mathbf{P})$$

化学反应中的波动方程

$$P_{mix}(t) = \varepsilon_0 \beta(t) * E(t) = \varepsilon_0 \chi(t) \frac{1}{\tau_{mix}} e^{-\frac{t}{\tau_{mix}}} * E(t)$$

其中 τ_{mix} 为混合物的弛豫时间

$$\Delta P(E, t) = \frac{\varepsilon_0 E}{kT} \left((c_1 \mu_A + c_3 \mu_B) e^{-\frac{t}{\tau}} + (c_2 \mu_A + c_4 \mu_B) e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{ch}}\right)t} \right)$$

化学反应中的波动方程

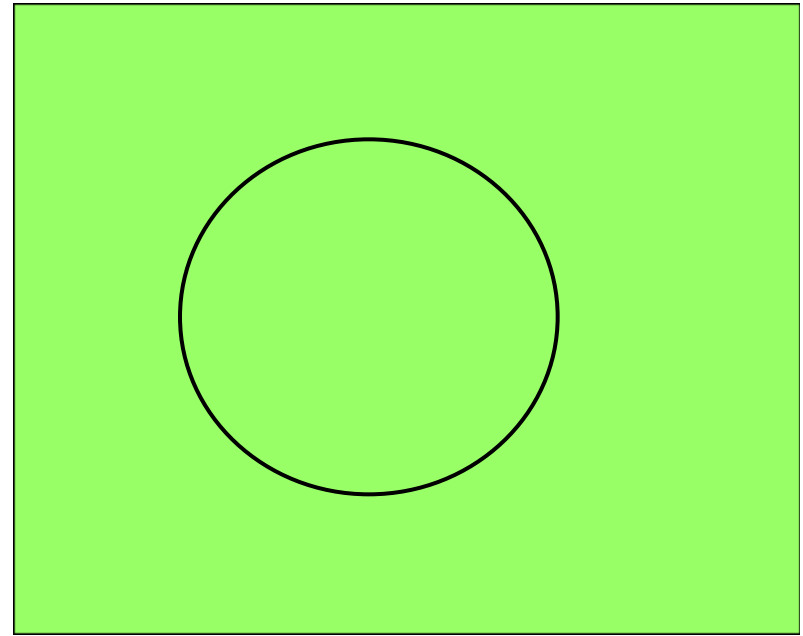
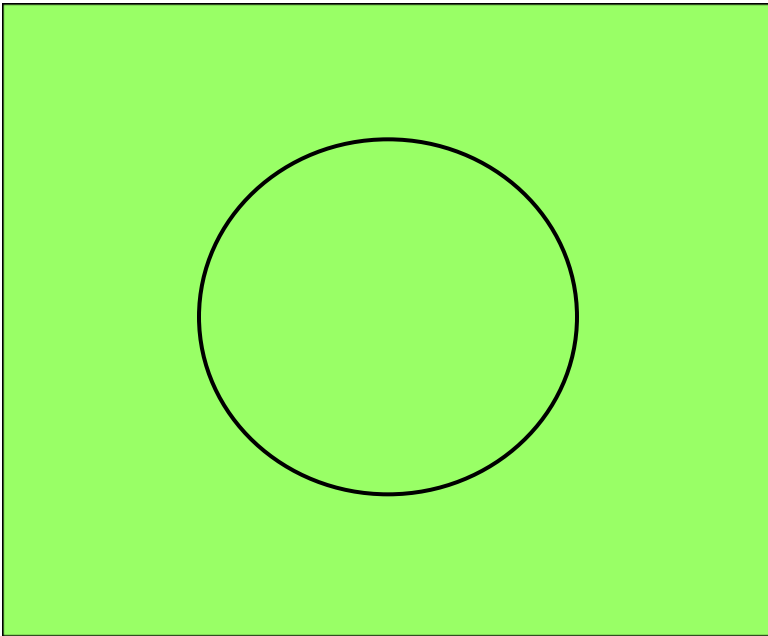
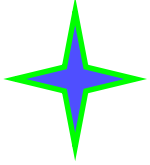
$$\nabla^2 \mathbf{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} + \mu_0 \varepsilon_0 \chi(t) \frac{1}{\tau_{mix}} e^{-\frac{t}{\tau_{mix}}} * \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

$$+ \mu_0 \varepsilon_0 \frac{\partial^2 \left\{ \left((c_1 \mu_A + c_3 \mu_B) e^{-\frac{t}{\tau}} + (c_2 \mu_A + c_4 \mu_B) e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{ch}}\right)t} \right) \frac{\mathbf{E}}{kT} \right\}}{\partial t^2}$$

$$\nabla^2 \mathbf{H} = \mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{H}}{\partial t^2} + \mu_0 \varepsilon_0 \chi(t) \frac{1}{\tau_{mix}} e^{-\frac{t}{\tau_{mix}}} * \frac{\partial^2 \mathbf{H}}{\partial t^2}$$

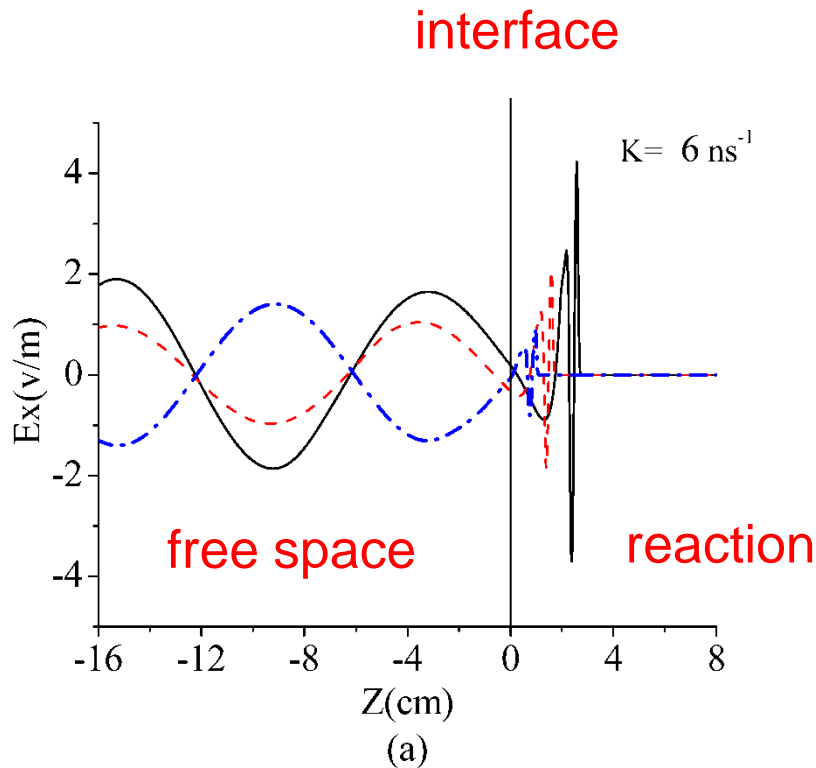
$$- \varepsilon_0 \frac{\partial}{\partial t} (\nabla \times \left\{ \left((c_1 \mu_A + c_3 \mu_B) e^{-\frac{t}{\tau}} + (c_2 \mu_A + c_4 \mu_B) e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{ch}}\right)t} \right) \frac{\mathbf{E}}{kT} \right\})$$

Simulation of microwave propagation in reactions

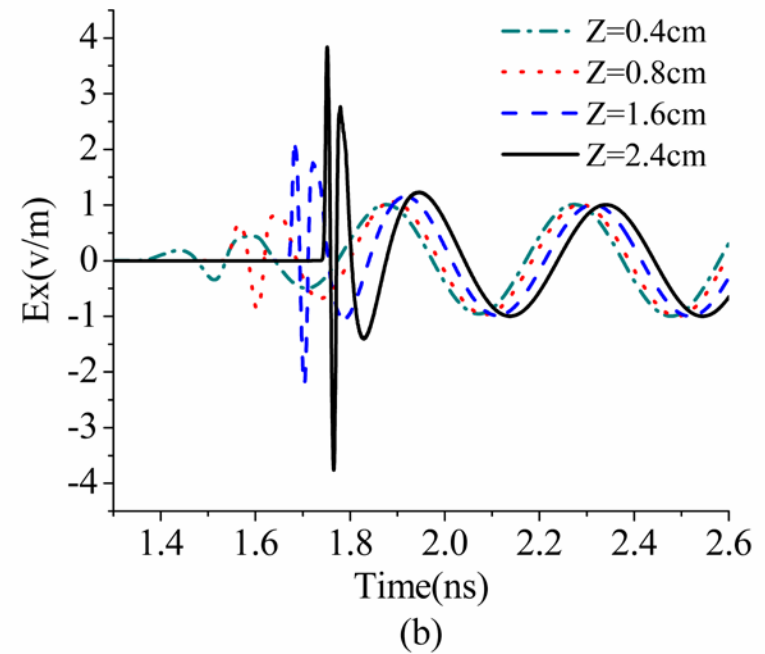


Microwaves penetrate into the media (2D) Microwaves penetrate into the reaction (2D)

Simulation of microwave propagation in reactions



E distribution



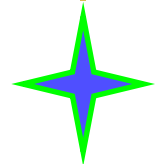
E with t (ns)

Outline

1. 微波化学中的非线性响应
2. 微波对氢键的作用
3. 化学极化增量
4. 化学反应中的波动方程
5. 结论

Conclusion

1. 微波在化学工业中的应用促使我们必须深入研究微波与化学反应之间的相互作用。
2. 微波场中化学反应极化的非线性特点导致微波在反应中的传播非常复杂。
3. 我们必须发展经典的电磁理论才能彻底理解微波与化学反应之间的相互作用。



Thank you for your
attention

